Correction to the Wills-Harrison approach: Influence on the Fe-based liquid alloys thermodynamics

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Abstract. Concentration dependencies of the Helmholtz free energy of mixing for liquid Fe-Co and Fe-Ni alloys are calculated near their melting temperatures in the framework of modified by us earlier the Wills-Harrison model at different values of the probability that not only diagonal couplings between *d* states in different atoms are possible in transition metal. It is found that an account of non-diagonal *d*-*d* couplings leads to an improvement of theoretical results for thermodynamic properties of liquid transition-metal binary alloys.

1. Introduction

The knowledge of physical-chemical properties of melts containing transition metals plays an important role for investigations of metallurgical processes and understanding the characteristics of produced steels and alloys. Among different theoretical approaches for studying the melts of transition metals (for example, at last years, [1-8]; see also the review [9]), the Wills-Harrison (WH) approach [10] is one of the most successful. The WH model is based on the Harrison-Froyen [11] approximation which introduces some elements of the muffin-tin orbital theory [12] into transition-metal pseudopotential theory [13, 14], the rectangular model for density of *d* states [15] and the simple-metal pseudopotential theory which works in the framework of the nearly-free-electron (NFE) approximation [16].

In works [10, 11] the diagonal matrix elements with respect to the magnet quantum number, *m*, between *d* states of neighboring atoms are taken into account only. It is truly in the case of the rotational symmetry with axis along the interatomic distance. Since the *d*-electron contribution to the potential energy, E_d, is non-pairwise in principle, the named above symmetry should be disturbed and non-diagonal *d*-*d* couplings may arise.

Recently, we suggested the correction of the WH model taking into account non-diagonal couplings between *d* states in transition metals [17] and applied this correction to study the WH effective pair interaction in pure liquid Fe, Co, Ni [17] and equiatomic Co-Ni liquid alloy [18]. In the present work, using the variational method [19] with the additive hard-sphere (HS) reference system [20] we investigate how this correction influences on the thermodynamic properties of binary liquid alloys of transition metals.

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2. Theory

The Helmholtz free energy per atom, F, of the binary liquid alloy described by the WH approximation in the framework of the HS variational method is calculated by minimization of

$$F_{\text{var-HS-WH}} = F_{\text{HS}} + U_e - TS_e + \langle E_d \rangle_{\text{HS}} + \frac{2\pi}{\Omega}\sum_{i,j=1}^{2} c_i c_j \int_{\sigma_{ij}}^{\infty} \varphi_{ij\text{NFE}}(r) g_{ij\text{HS}}(r) r^2 \mathrm{d}r \quad (1)$$

with respect to the partial HS diameters, σ_{ij}. Here, U_e is the *s*-electron contribution to the internal energy; S_e is the electron entropy; T is the temperature; $\langle E_d \rangle_{\text{HS}}$ is the average of E_d over the HS reference system; Ω is the mean atomic volume; c_i is the concentration of the *i*-th component; $g_{ij}(r)$ is the partial pair correlation function; $\varphi_{ij}(r)$ is the partial pair potential (hereafter, all formulas are written in atomic units (a.u.)):

$$\varphi_{ij\text{NFE}}(r) = \frac{z_{si} z_{sj}}{r} + \frac{\Omega}{8\pi^2}\int_0^{\infty} F_{ij}(q)\frac{\sin(qr)}{qr} q^2 \mathrm{d}q \ , \quad (2)$$

where z_{si} is the effective number of valence *s* electrons per ion in the pure metal of the *i*-th kind; $F_{ij}(q)$ is the partial energy wave-number characteristic:

$$F_{ij}(q) = -\frac{\Omega q^2 \omega_i(q)\omega_j(q)}{8\pi[(\varepsilon(q)-1)^{-1} + 1 - f(q)]} \ , \quad (3)$$

where $\omega_i(q)$ is the form-factor of the unscreened *i*-th-kind ion pseudopotential; $\varepsilon(q)$ is the Hartree dielectric function; $f(q)$ is the exchange-correlation function used here in the Vashishta-Singwi form [21].

We use suggested specially for transition metals the Bretonnet-Silbert (BS) [22] local model pseudopotential generalized to binary alloys [23]:

$$\omega_{i\text{BS}}(r) = \begin{cases} \sum_{n=1}^{2} B_{ni} \exp\left(\frac{r}{na_i}\right), & r \le R_{\text{C}i} \\ -z_{si}/r, & r \ge R_{\text{C}i} \end{cases} \ , \quad (4)$$

$$\omega_{i\text{BS}}(q) = \frac{4\pi a_i^3}{\Omega}\left[\frac{B_{1i}J_{1i}(q)}{(1+a_i^2q^2)^2} + \frac{8B_{2i}J_{2i}(q)}{(1+4a_i^2q^2)^2}\right] - -\frac{4\pi z_{si}\cos(qR_{\text{C}i})}{\Omega q^2} \ , \quad (5)$$

where $R_{\text{C}i}$ and a_i are pseudopotential parameters;

$$B_{1i} = (z_{si}/R_{\text{C}i})[1 - 2a_i/R_{\text{C}i}]\exp(R_{\text{C}i}/a_i) \ ; \quad (6)$$

$$B_{2i} = (2z_{si}/R_{\text{C}i})[a_i/R_{\text{C}i} - 1]\exp(0.5R_{\text{C}i}/a_i) \ ; \quad (7)$$

$$J_{1i}(q)=2-\frac{1}{e^{(R_{Ci}/a_i)}}\left\{\left[R_{Ci}\frac{1+a_i^2q^2}{a_i}+1-a_i^2q^2\right]\frac{\sin(qR_{Ci})}{a_iq}+\left[2+\frac{R_{Ci}(1+a_i^2q^2)}{a_i}\right]\cos(qR_{Ci})\right\}; \quad (8)$$

$$J_{2i}(q)=2-\frac{1}{e^{(R_{Ci}/2a_i)}}\left\{\left[R_{Ci}\frac{1+4a_i^2q^2}{2a_i}+1-4a_i^2q^2\right]\frac{\sin(qR_{Ci})}{2a_iq}+\left[2+\frac{R_{Ci}(1+4a_i^2q^2)}{2a_i}\right]\cos(qR_{Ci})\right\}. \quad (9)$$

The expression for the structure-dependent *d*-electron energy of the binary mixture was obtained in [24]:

$$\left\langle E_d\right\rangle_{\mathrm{HS}}=-\frac{\sqrt{12}K_b\bar{z}_d}{2}\left(\frac{10-\bar{z}_d}{10}\right)\left(\frac{4\pi}{\Omega}\sum_{i,j=1}^{2}\frac{c_ic_j(r_{di}r_{dj})^3}{7\sigma_{ij}^7}+\frac{2}{\pi}\sum_{i,j=1}^{2}\sqrt{c_ic_j}\,r_{di}^3r_{dj}^3\int_0^\infty\left[S_{ij\mathrm{HS}}(q)-\delta_{ij}\right]q\mathrm{d}q\int_{\sigma_{ij}}^\infty\frac{\sin(qr)}{r^9}\mathrm{d}r\right)^{\frac{1}{2}}$$

$$+\bar{z}_dK_c\left(\frac{2\pi}{\Omega}\sum_{i,j=1}^{2}\frac{c_ic_j(r_{di}r_{dj})^3}{5\sigma_{ij}^5}+\frac{1}{\pi}\sum_{i,j=1}^{2}\sqrt{c_ic_j}\,r_{di}^3r_{dj}^3\int_0^\infty\left[S_{ij\mathrm{HS}}(q)-\delta_{ij}\right]q\mathrm{d}q\int_{\sigma_{ij}}^\infty\frac{\sin(qr)}{r^7}\mathrm{d}r\right), \quad (10)$$

where $\bar{z}_d=c_1z_{d1}+c_2z_{d2}$; z_{di} is the effective number of valence *d* electrons per ion in the pure metal of the *i*-th kind, $z_{di}=z_i-z_{si}$ (z_i is the total number of valence electrons per *i*-th kind ion); r_{di} is the *d*-state radius of the free atom of the *i*-th kind; $S_{ij\mathrm{HS}}(q)$ is the partial structure factor in the Ashcroft-Langreth analytical form [25]; δ_{ij} is the Kronecker symbol; K_b and K_c are coefficients arising in the result of summarizing the *d-d* matrix elements. When the orbital quantum number is equal to two (that corresponds to the case of the *d*-band metal), these coefficients within the traditional WH model [10] are

$$K_b=28.06/\pi \quad , \quad (11)$$

$$K_c=225/\pi^2 \quad . \quad (12)$$

In [17] were obtained the expressions of K_b and K_c for a general case, when the non-diagonal *d-d* couplings can take place in principle:

$$K_b=\left[\frac{1}{5}\left(\left(1-\frac{4p}{5}\right)y_0^2+\left(2-\frac{6p}{5}\right)(y_2^2+y_1^2)+\frac{4p}{5}y_0(y_1+y_2)+\frac{8p}{5}y_1y_2\right)\right]^{\frac{1}{2}}, \quad (13)$$

$$K_c=-\frac{2}{5}\left[\left(1-\frac{4p}{5}\right)y_0x_0+\left(2-\frac{6p}{5}\right)(y_1x_1+y_2x_2)+\frac{2p}{5}(y_0(x_1+x_2)+x_0(y_1+y_2))+\frac{4p}{5}(y_1x_2+y_2x_1)\right]$$

(14)

where p is the probability that any from all 25 equiprobable *d-d* couplings can be realized between two neighboring atoms in metal; $(1-p)$ is the probability that any from 5 diagonal couplings only are possible; y_m and x_m ($y_m = y_{|m|}$ and $x_m = x_{|m|}$) are the combinatoric coefficients:

$$y_m = -\frac{(-1)^{|m|}180}{\pi(2+|m|)!(2-|m|)!}\ , \tag{15}$$

$$x_m = -\frac{1}{8}\left(1+\frac{4m^2-1}{9}\right)y_m\ . \tag{16}$$

At $p=0$ Eqs. (13) and (14) are transformed to Eqs. (11) and (12), respectively.

3. Results and Discussion

Earlier, in the framework of the WH model we calculated the concentration dependencies of the Helmholtz free energy of mixing, ΔF, for liquid Fe-Co [24] and Fe-Ni [26] alloys at $T=1863\text{K}$. Here, these dependencies at different values of p are considered.

Values of r_{di}, z_{si}, R_{Ci}, and a_i are taken the same as values of r_d, z_s, R_C, and a for corresponding pure metals from the works of Wills and Harrison [10] for r_{di} and Jakse and Bretonnet [27] for other parameters (Table 1). The mean atomic volume for each alloy composition is calculated by means the minimization of $F_{\text{var-HS-WH}}$ with respect to Ω.

The calculated concentration dependencies of ΔF in comparison with experiment [28] are presented in Figs. 1, 2. It is observed that the better agreement with experimental data among used values of p is achieved at $p=0.75$.

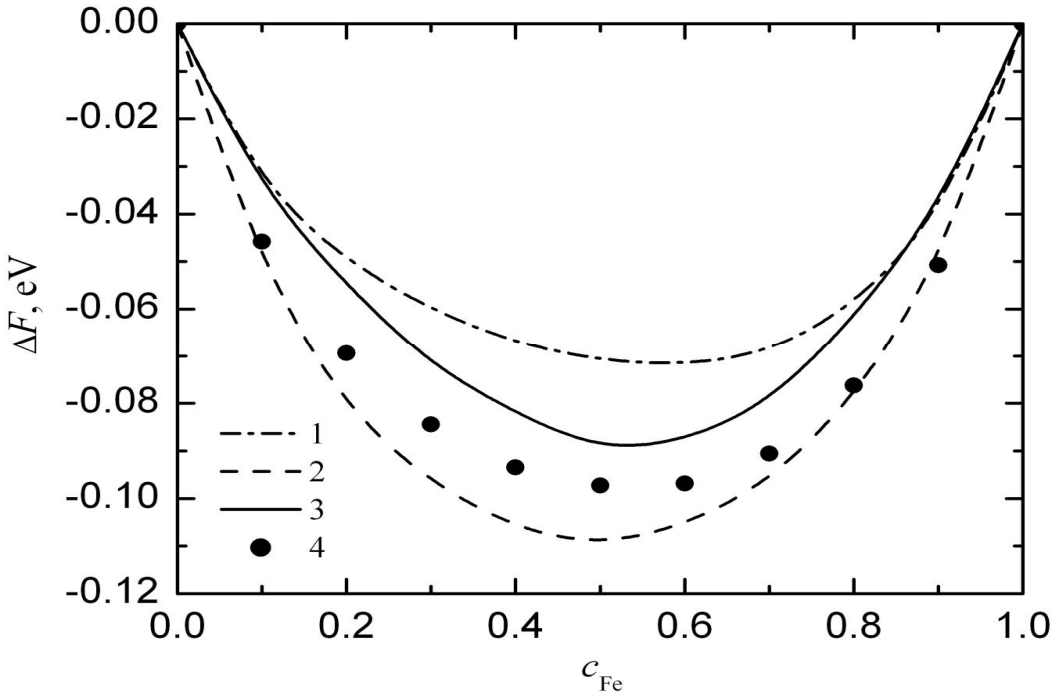

Figure 1. The Helmholtz free energy of mixing of liquid Fe-Co alloy at $T=1863\text{K}$
(1): $p=0$; (2): $p=1$; (3): $p=0.75$; (4): experiment

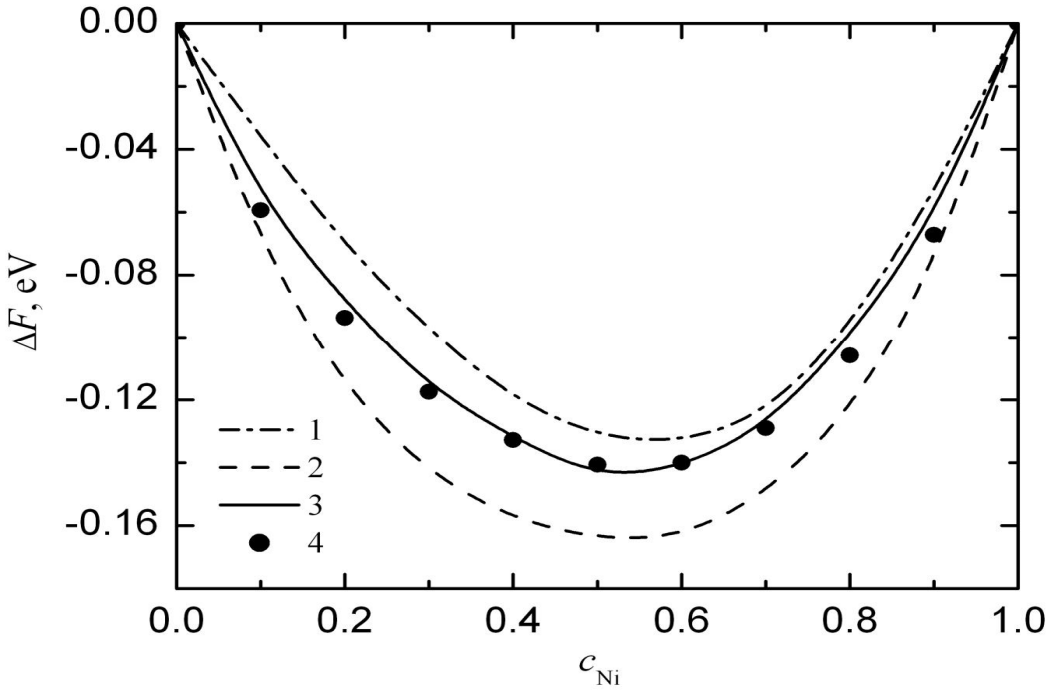

Figure 2. The Helmholtz free energy of mixing of liquid Fe-Ni alloy at $T = 1863\text{K}$
(1): $p = 0$; (2): $p = 1$; (3): $p = 0.75$; (4): experiment

Table 1. Input parameters for the calculation

	Fe	Co	Ni
r_{di} (a.u.)	1.512	1.437	1.342
z_{si}	1.4	1.4	1.4
z_{di}	6.6	7.6	8.6
R_{Ci} (a.u.)	1.540	1.641	1.030
a_i (a.u.)	0.363	0.393	0.207

4. Conclusion

The results obtained show that the account of non-diagonal *d-d* couplings within the Wills-Harrison model leads to an improvement of theoretical results for thermodynamic properties of liquid transition-metal binary alloys. In the further study it is necessary to find a method determining values of the probability p for different transition metals and alloys *a priory*.

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